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[A REPORT OF THE SPECIAL COMMITTEE ON ENVIRONMENTAL STANDARDS
OF NITROGEN OXIDES AND OTHER POLLUTANTS]

Central Council for Pollution Countermeasures, Department of Atmosphere
and Special Committee on Environmental Standards of
Nitrogen Oxides and Other Pollutants

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A REPORT OF THE SPECIAL COMMITTEE ON ENVIRONMENTAL STANDARDS
OF NITROGEN OXIDES AND OTHER POLLUTANTS

Central Council for Pollution Countermeasures, Department of Atmosphere
and Special Committee on Environmental Standards of
Nitrogen Oxides and Other Pollutants

The Special Committee on Environmental Standards of Nitrogen Oxides and Other Pollutants reports the following to the Department of the Atmosphere of the Central Council for Pollution Countermeasures.

1. INTRODUCTION

Nitrogen oxides and other pollutants here include nitrogen oxides (NO_x), photochemical oxidants, and ozones.

Among the nitrogen oxides, nitric oxide and nitrogen dioxide are especially important in their effects on human beings and their environment. Nitrogen oxides are also generated in natural phenomenon such as the metabolism of soil microorganisms. According to the measurements heretofore, nitrogen dioxide concentration in the atmosphere is less than 0.003 ppm. Less than 0.05 ppm of ozone is present on the earth's surface due to such things as its descent from the stratosphere.

Nitric oxide (NO) is generated from so-called fixed sources such as steam-power plants and furnace operations and from so-called moving sources such as automobiles, by air being heated at high temperature, and is released into the atmosphere. Nitric oxide is oxidized in the atmosphere, resulting in nitrogen dioxide (NO₂). Besides the above sources, nitrogen oxides are released directly into the atmosphere from such things as the nitrification process in the chemical industry. From the various causes above, nitrogen

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oxides lead to the regional and local atmospheric pollutions. The atmospheric pollution due to nitrogen oxides in Japan has rapidly worsened in the past ten years.

When nitrogen dioxide and hydrocarbon, non-saturated hydrocarbon in particular, coexist and are irradiated by sunlight, atmospheric pollutants are generated secondarily. When sulfur dioxide is present, it is oxidized and sulfuric acid mist is generated. In this case, atmospheric pollution due to photochemical reactions is further worsened.

Today, both nitric oxide and nitrogen dioxide together are generally called nitrogen oxides. Nitrogen oxides not only affect the health of human beings but also cause an impairment of distant vision and coloration of the atmosphere (reddish brown color).

The knowledge we have today on the effects on human beings is mainly on nitrogen dioxide; the knowledge on nitric oxide is still insufficient. Therefore, we are recommending environmental standards for nitrogen dioxide. We hope to obtain more data necessary for the establishment of environmental standards for nitric oxide from future research.

On the other hand, the following products of photochemical reaction involving both nitrogen dioxide and hydrocarbon in the atmosphere are currently drawing attention: oxidizing substances such as ozone (O_3), nitrogen dioxide, peroxyacetylnitrate (PAN) and its homologues, and peroxides, reducing substances such as formaldehyde and acrolein, aerosol, and very active free radicals which should be noted even though their effects are not yet clearly established. The effects caused by the combination of these are generally called the effects of photochemical oxidants.

Besides affecting the health of human beings such as irritating mucous membranes, violent effects on respiratory organs, and effects on other tissues and organs, the effects of photochemical oxidants are observed in rubber cracks, adverse effects on plants, damage to agricultural products, and discoloration of clothes.

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The authors

We define photochemical oxidants as oxidizing substances, exclusive of nitrogen dioxide, which are generated by the photochemical reaction. This is based on the method of measurement, using neutral potassium iodide solution, which will be mentioned later. It has been confirmed that, in this case, most of the measured values are due to ozone. Consequently, under the cognition that most of photochemical oxidants are ozones, we recommend the environmental standards of photochemical oxidants as an index of photochemical-reaction-generated pollutants.

2. METHOD OF MEASUREMENT

In the measurement of nitrogen oxides and other pollutants, a method which makes it possible to follow regional atmospheric pollution due to these pollutants must be adopted. However, there are cases where the source of nitrogen oxide generation is a moving one, and the pollution condition which is directly affected by the generating source may have to be measured.

In the latter case also, the relationships between the source and its effects, rather than the generating source, should be elucidated.

2.1. Measurement Location

The measurement of nitrogen oxides and other pollutants must be conducted at such a location that the measurement results are effectively utilized in describing the pollution and the trend due to these pollutants, in the determination of its effects, in the establishment of countermeasures against this pollution, and in the evaluation of their effectiveness.

The collection of air samples should be performed at the height where the human beings breathe, more than 1.5 m and less than 10 m above the ground in principle.

Since the measured value of photochemical oxidants has to be compensated for nitrogen oxides, nitrogen oxides must be measured where photochemical oxidants are measured.

2.2.1. Measurement of Nitrogen Oxides

2.2.1.1. General remarks

It is desirable to continuously measure nitrogen dioxide. The measured results are arranged in one hour units. A scale range for the measurement device is selected based on the atmospheric concentration of nitrogen dioxide, but, generally, one which can measure from several ppb to 2 ppm is appropriate.

In order to clarify the condition of pollution due to nitrogen oxides, it is desirable to measure not only nitrogen dioxide but also nitric oxide.

2.2.1.2. Standard method

The measurement based on the extinction photometer is made the standard method in the determination of nitrogen oxides concentration. However, other methods which can demonstrate that the equivalent measurement results can be obtained may be used.

2.2.2. Measurement of Photochemical Oxidants

2.2.2.1. General items

Oxidant is a general term for an oxidizing substance which frees iodide from neutral potassium iodide solution. Photochemical oxidants are measured by utilizing this reaction.

Photochemical oxidants are preferably measured continuously. The measurement results are to be arranged in units of one hour.

The measurement device which can measure in the concentration range between several ppb to 1 ppm is appropriate.

2.2.2.2. Standard method

The measurement based on extinction photometer using the neutral potassium iodide solution is made the standard method in the determination of photochemical oxidants. However, other methods which can demonstrate that the equivalent measurement results can be obtained, the coulometric method for example, may be used.

In the standard method, the measured value of oxidants is compensated for nitrogen dioxide concentration. As this method is affected by reducing substances such as sulfur dioxide, a scrubber containing chrome trioxide is used to remove their interference. Since nitric oxide in the atmosphere is oxidized into nitrogen dioxide and affects the measured value of oxidants, a compensation must be made for nitric oxide concentration also.

Most of oxidant concentration compensated for by nitrogen oxide concentration are assumed to be due to ozone.

2.2.3. Measurement of Ozones

As mentioned already, when photochemical oxidants are measured by the standard method, most of them are ozones. It is clear that the direct measurement of ozones is desirable. As the method of determination of ozones which can be used today, there is a chemical radiation method which utilizes the reaction with ethylene. This method can measure ozone selectively without being affected by sulfur dioxide or nitrogen dioxide. Since it is gradually being put into a practical usage, we hope it will be adopted as the standard method, after accumulating on-site experiences in the future.

2.3. Addendum

It is necessary to perfect the research data for judging the effects and the pollution conditions of atmospheric pollution by nitrogen oxides and other pollutants. In conjunction with an increased practical application of

the method of selective measurement of nitric oxide and ozone, we strongly hope that these measurement methods will be used together with the standard methods mentioned above.

Further, in conjunction with the mechanism of photochemical oxidant generation, we strongly hope that hydrocarbon measurements will be started soon as a daily task.

3. EFFECTS ON HUMAN BEINGS

3.1. Effects of Nitrogen Oxides

Because of the difficulty in an experimental technique, sufficient knowledge has not been yet obtained concerning the effects of nitric oxide. When animals are exposed to an extremely high concentration of nitric oxide, convulsions and paralysis due to the impairment of the central nervous system appear. Affinity with hemoglobin is strong; in a test tube experiment, it was found to be several hundred times that of carbon monoxide. The growth of nitric oxide hemoglobin and methemoglobin has been recognized in a high concentration animal experiment. Although a sufficient knowledge on its effect on human beings is unavailable, it may turn out, as a result of the future research activities, that nitric oxide must be viewed more seriously than nitrogen dioxide.

Nitrogen dioxide has the property of easily reaching deep inside the respiratory organs regardless of the presence of suspended particulate matter. When it coexists with suspended particulate matter, the synergistic action of nitrogen dioxide and suspended particulate matters, an increase in the air flow resistance in the air passages in the living body, has been confirmed in experiments with humans.

Nitrogen dioxide has been known for a long time as an irritant gas for the respiratory organs, and this poisoning has been drawing attention as an occupational disease. In animal experiments also, the cause of death in an

acute nitrogen dioxide poisoning of an occupational level concentration is attributed to pulmonary edema and others, while chronic bronchitis and pulmonary emphysema are considered as chronic effects.

Man can sense the odor of 0.12 ppm nitrogen dioxide. This olfactory value decreases when sulfur dioxide is also present.

A significant rise in the air flow resistance of the human air passage is found after a 10 minute exposure of 16.6 ppm nitrogen dioxide. Further, a synergistic action has been found for sulfur dioxide and nitrogen dioxide when the reaction of an increase of the air flow resistance occurs.

In animal experiments, the effects on pulmonary cells are observed for 0.5 ppm exposure for 4 hours, bronchiolitis and pulmonary emphysema are observed for 0.5 ppm exposure for several months.

In animal experiments, an increased sensitivity to pneumobacillus and influenza virus, a shortened life span, and a weakened ability to eliminate bacteria are indicated under the exposure to nitrogen dioxide. For example, when infected with pneumobacillus under the 0.5 ppm exposure for 12 months, an increase in fatality and a weakening in the ability to eliminate bacteria are found.

When one is infected with influenza virus because of 10 ppm nitrogen dioxide exposure for 2 hours a day, interstitial pneumonia is observed, and its pathological findings increase with an increased number of days of exposure. Further, the 0.5 ppm exposure for 6 months results in a multiplication of epithelial cells in the peripheral bronchi and a mild pulmonary emphysema. When infected with influenza virus in addition, the pneumonia becomes more serious and an adenomatous multiplication of epithelial cells in the peripheral bronchi appears. This adenomatous multiplication should be carefully observed.

The possibility of nitrogen dioxide being a cause of bronchial asthma has been shown in animal experiments. An increase in the growth of carbon monoxide hemoglobin has also been reported in animal experiments, when carbon monoxide is also present.

There has been very little study of acute or chronic effects which appear among the residents at current levels of concentration.

A rise in influenza infection and absenteeism of school children in areas with nitrogen dioxide and nitrate pollution, but almost no sulfur dioxide pollution, was reported in the United States. The concentrations of nitrogen dioxide and suspended nitrates in this case were 0.062-0.109 ppm and $3.8 \mu\text{g}/\text{m}^3$ or more, respectively. The survey on the school children in the area where sulfur dioxide pollution and nitrogen dioxide pollution coexist is being conducted in Czechoslovakia.

As mentioned already, the synergistic action of nitrogen dioxide with sulfur dioxide should be carefully observed. In Japan, pollution by nitrogen dioxide only is an exceptional local case. Since, in most cases, both are present, the study on the environmental standards of nitrogen dioxide cannot be performed by ignoring the presence of sulfur dioxide.

Epidemiological study of the percentage of those affected with chronic bronchitis has produced many findings in recent years. Among the findings, approximately 3% of adults over 40 years old in non-polluted areas were affected with chronic bronchitis. More than 5% of male government employees in Tokyo (1968-1971), in the area where the yearly average value of the 24 hour average concentration of sulfur dioxide was less than 0.05 ppm, were affected with persistent coughing and expectoration (simple chronic bronchitis). The yearly average value of the 24 hour average concentration of nitrogen dioxide in this case was more than 0.042 ppm.

According to the survey of housewives over 30 years old conducted in 6 locations in Japan during the winter of 1970 to 1971, a high correlation was

found between the percentage of those affected with persistent coughing and expectoration and the concentration of nitrogen dioxide. The concentration of nitrogen dioxide was measured for 8-72 hours per month over 3 months. In the area where the percentage of those affected with persistent coughing and expectoration exceeded 4%, one hour average of the nitrogen dioxide concentration was 0.029 ppm. It is widely recognized that the percentage of those affected is smaller for adult females than for adult males.

3.2. Effects of Photochemical Oxidants

The effects of photochemical oxidants are similar to but stronger than those of nitrogen oxides.

Since most of photochemical oxidants are ozones, we shall look at the effects of ozone.

As far as animal experiments are concerned, the absorption of ozone in the upper air passage is low, and ozone easily reaches deep inside the respiratory organs. For 1 ppm exposure for 4 hours, a mild pulmonary edema is observed 20 hours after exposure. Under the long period exposure, bronchitis, bronchiolitis, pulmonary emphysema, pulmonary fibrosis, and adenoma are observed. Under the 0.25-0.5 ppm exposure for 3 hours, a rise in the air flow resistance is observed. Under the 1 ppm exposure for one hour, the effects which presumably represent change in proteins of lung cells are recognized. The ozone toxicity increases for animals which have performed exercise.

An increase in sensitivity to bacterial infection due to ozone is the same as nitrogen dioxide; it is recognized already under the 0.08 ppm exposure for 3 hours. The fact that the possibility of ozone being a cause for bronchial asthma is greater than that of nitrogen dioxide has been confirmed in animal experiments.

In animal experiments, the appearance of resistivity against acute exposure has been observed, but it is not known for chronic exposure.

In human experiments of ozone exposure, no clear effects were observed with the acute exposure of 0.1 ppm for one hour. For 0.5-1.0 ppm exposure for 1-2 hours, an increase in the airway resistance, a decrease in the carbon monoxide diffusion capacity of the lungs, and a decrease in the capacity of the lungs are observed, and these symptoms worsen with exercise. The above are average reactions and individual differences do exist. Therefore, attention should be paid to persons with high sensitivity.

In the long exposure of ozone to human beings, no clear effects were found among the factory workers with less than 0.2 ppm exposure. At 0.3 ppm, there was an irritation of nose and pharynx. Under 0.5 ppm exposure for 3 hours a day, 6 days a week for 12 weeks, a lowering in the pulmonary ventilation ability is recognized.

Also, at 0.02 ppm, man can smell the ozone odor.

The above are the results of the laboratory study. The effects on the residents when photochemical oxidants are actually generated and other atmospheric pollutants are also present are as follows.

According to the study in the United States, damages to plants appear for 0.05 ppm exposure for 4 hours. Eye irritation occurs under the 0.1 ppm exposure for a short period of time. The frequency of spasms of the asthmatic patients increases at a peak concentration of 0.13 ppm. This is roughly equivalent to the one hour average concentration of 0.05-0.06 ppm. There is also a report that the chronic respiratory symptoms worsen at the one hour average concentrations of 0.2-0.7 ppm, but not at 0.06 ppm. The results of cross country event drop in a statistically significant way when the average concentration one hour before the start is 0.03-0.30 ppm.

The reports on the effects of photochemical oxidants on the local residents in Japan are still not sufficient. At about 0.10 ppm photochemical

oxidant concentration, damages to agricultural products and plants and eye irritations have been reported by the residents. As was seen in animal experiments with ozone, the effects during exercises cannot be ignored. In fact, there have been frequent reports of harm to students during exercise. In the summer of 1971, the violent irritations of the eye and respiratory organs and abnormal findings of the clinical tests were found among the exercising players during the so-called photochemical smog episode in the southern part of Osaka Prefecture.

The concentrations over one hour of various pollutants at that time were more than 0.2 ppm ozone, more than 0.05 ppm sulfur dioxide, 6-10 $\mu\text{g}/\text{m}^3$ sulfuric acid mist, and 0.05 ppm nitrogen dioxide.

3.3. Addendum

The effects of nitrogen dioxide, ozone, and photochemical oxidant on the human life environment are discomfort, odor, distant vision impairment, cracks in rubber, and plant damage.

Since the first consideration of the effects of nitrogen dioxide, ozone, and photochemical oxidants is on the respiratory organs, especially the lungs, the emphasis was placed on their effects. We would like to point out that, depending on the product of the exposure period and the concentration of these pollutants, there is a concern about the effects on various organs such as kidney, liver, heart, cerebra, and blood, and about effects such as mutations and cancerous growth.

4. CONCLUSIONS

Concerning the concentration of nitrogen dioxide and photochemical oxidants in the atmosphere which should always be maintained throughout the year, we propose the following based on the previously mentioned measurement methods and the data on the effects on human health:

1) In regard to nitrogen dioxide, the 24 hour average of one hour values is to be less than 0.02 ppm, taking into consideration its effects, especially the chronic effects, and the synergistic action with sulfur dioxide.

2) In regard to photochemical oxidants, the one hour average value is to be less than 0.06 ppm, taking into consideration the prevention of short period exposure effects.

This report is a result of the study we have performed based on the data obtained up to now, and is a proposal for determining nitrogen dioxide and photochemical oxidants.

Efforts must be made for the advancement in the study of the measurement method and the effects, especially the enrichment of data related to the effects of complex pollution, and the effects of nitric oxide, hydrocarbon, ozone, and other photochemically reacting substances. Progress in the method of environmental concentration measurement are necessary.

This report should be modified periodically in the future based on the results of the study accompanying the progress of research in the evaluation of the effects on human beings and various objects related to human beings, the determining conditions, and the change in the evaluation and cognition of health.

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The methods of measurement of nitrogen oxides and other pollutants in
this report have been summarized from the study made by the Committee on the
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